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END-OF-YEAR REPORT

1 June 1989 - May 31, 1990

PUBLICATIONS/PATENTS/PRESENTATIONS/

HONORS/STUDENTS REPORT

For

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IMAGING AND SPECTROSCOPY OF SMALL MOLECULES

BY SCANNING TUNNELING MICROSCOPY

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Submitted

May 25, 1990

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End-of-Year Report 1June 1989 - 31 May 1990

PART I

a. Papers submitted:

1. R. J. Driscoll, M. G. Youngquist, J. D. Baldeschwieler, "Atomic-Scale Imaging of DNA Using Scanning Tunneling Microscopy," accepted *Nature* (1990).
2. M. G. Youngquist, R. J. Driscoll, *Scientific Correspondence*, submitted *Nature* (1990).

b. Papers published:

1. R. J. Driscoll, M. G. Youngquist, J. D. Baldeschwieler, "Scanning Tunneling Microscopy of DNA and Polynucleotides," *Bull.Am.Phys.Soc.* 35(3), 649 (1990).
2. M. G. Youngquist, J. D. Baldeschwieler, "Scanning Tunneling Microscopy of Molybdenum Disulfide," *Bull.Am.Phys.Soc.* 35(3), 227 (1990).

c.-g. None

h. Invited Presentations:

1. Shenda M. Baker, "Seeing Atoms by Scanning Tunneling Microscopy," invited seminar at Harvey Mudd College, Claremont, CA, April 1990.
2. T. R. Coley, W. A. Goddard III, J. D. Baldeschwieler, "Interpreting STM Images of Transition Metal Dichalcogenides: Guidance From Theory," invited talk, Aerospace Corporation, El Segundo, CA, February 1990.

i. Contributed presentations:

1. T. R. Coley, J. D. Baldeschwieler, "Ab Initio Calculations for Describing STM Images of MoS₂ and MoTe₂," contributed oral, STM'90 NANO Conference, Baltimore, MD, July 1990.
2. John Kramar, Michael Weimer, John D. Baldeschwieler "Band Bending and the Apparent Barrier Height in Tunneling Microscopy," contributed oral, American Physical Society 35th National Symposium, St. Louis, Missouri, March 1989.

American Physical Society Meeting, Anaheim, CA, March 1990:

3. R. J. Driscoll, M. G. Youngquist, J. D. Baldeschwieler, "Scanning Tunneling Microscopy of DNA and Polynucleotides."
4. M. G. Youngquist, J. D. Baldeschwieler, "Scanning Tunneling Spectroscopy of Molybdenum Disulfide."

- j. **Honors/Awards** - Tolman Medal Award, American Chemical Society, 1989
Nicols Award, American Chemical Society, 1990
- k. **Number of graduate students receiving at least 25% support on ONR grant:**
Total 5 Minorities - Asian * 2
- Shenda Baker Terry Coley Michael Youngquist
*David Baselt *Robert Driscoll
- l. None
- m. Other Funding

<u>Agency</u>	<u>Grant Title</u>	<u>Annual Total Direct Costs</u>	<u>Period of Support</u>
ARO DAAL03-87-K-0044	Development of Micro- encapsulation Techniques	60,125	3/15/89- 3/14/90
ONR N00014-88-K-0214	Imaging & Spectroscopy of Small Molecules by STM	73,645	10/1/89- 9/30/90
Amer. Cancer Society	Liposomal Mediated Tumoricidal Activation of Monocytes	64,000	7/1/89- 6/30/90
NSF	Localized Detection of Inelastic Electron Tunneling Using STM	79,356	2/1/90- 1/31/91
Ford Motor Co.	Atomic Scale Friction	40,000	4/1/90- 3/31/91



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- a. **Dr. John D. Baldeschwieler**
- b. **(818)356-6088**
- c. **Dr. Mark Ross**
- d. **Brief description of project:**

The principal objective of our ongoing ONR program is to investigate the imaging of molecular adsorbates by scanning tunneling microscopy (STM), in an attempt to understand the nature of the electronic interaction between molecules and substrate surfaces. We proposed to determine the contrast mechanism involved in imaging adsorbates. We have made significant progress in this effort, using STM to image DNA. In addition, we continue our investigations on cleaved GaAs, MoS₂ and the reactions of small molecules on 7x7 reconstructed silicon(111) surfaces, as well as a parallel theoretical modeling effort.

e. Significant results during the past year:

We have used our ultra-high vacuum (UHV)-STM to image for the first time an individual double helix of DNA with atomic resolution (1,2). In this study, DNA was deposited onto a highly oriented pyrolytic graphite (HOPG) surface without chemical modification and imaged with an STM to reveal structure down to the atomic-scale. The general features of the molecule including the base pairs are clearly resolved. Our images represent the highest magnification of a single molecule of DNA by any technique to date. Comparisons of the STM data to models of DNA based on x-ray crystallography provide convincing evidence of the atomic precision of these images. These results reveal the ability of STM to study local structural variations of DNA as well as exhibit the possibility of using STM to identify directly the base sequence which comprises the genetic code. In addition to topographical imaging, simultaneous measurement of the barrier-height (the barrier to quantum mechanical tunneling) reveals an interesting relationship between atomic-scale topography and barrier-height (see figures) which provides some insight to the STM imaging process of molecular adsorbates. Although the molecular energy levels of adsorbates are expected to be inaccessible to STM since they lie far in energy from the typical metal Fermi level, we have shown that it is possible to image even "large" adsorbates with atomic resolution. These results are consistent with the imaging mechanism introduced briefly in the last proposal. Because of the quantum-mechanical requirement of orthogonality between the combined wavefunction of an adsorbate and its substrate, the adsorbed molecule can modulate the exponentially-decaying tail of the substrate wavefunction in such a way as to impose structure on the available states of the substrate in the vicinity of the molecule.

Another goal of our last proposal was to explore the effects of surface defects on the electronic structure of semiconductors. To that end, we presented preliminary results on the imaging of cleaved GaAs(110). We continue to investigate the structural and electronic properties of semiconductor surfaces.

including the topography and spectroscopy of molybdenum disulfide (MoS_2), as extensively described in the previous proposal. Gallium arsenide (GaAs), a semiconductor of wide interest to industry for its unique electronic properties, is another material we are presently investigating. Our STM imaging efforts on GaAs have concentrated on studying the properties of surface defects; we have imaged both point defects (missing atoms or vacancies) and adsorbed contaminants and have studied their distinct surface electronic characteristics. Examples of these defects and their surface electronic properties are illustrated and explained in the figures (and figure captions) provided. In these images, we are able to study either the gallium or arsenic atomic surface, depending on the direction of the tunneling electrons.

All of the software development described in the previous proposal has been completed. Our data collection software has been enhanced to allow complete integration of imaging and current-voltage spectroscopy. We have added the capability to obtain current-voltage spectra during acquisition of a topographic image via a keyboard interrupt; this feature allows spectra to be obtained immediately upon identification of a topographic feature of interest. A more significant addition to our software makes possible the collection of an array of current-voltage spectra associated with specific pixels of a simultaneously obtained topographic image. Images of the tunneling density of states can then be constructed from the i-v array by plotting the current at a selected voltage level as a function of x, y position; the method was introduced by Tromp, Hamers, and Demuth, who called it current imaging tunneling spectroscopy (CITS)(3). We have improved our data processing software to support CITS requirements. In addition, the software now can be used to average selectively subsets of the i-v spectra; individual spectra obtained at similar surface sites can be averaged to generate one i-v with an improved signal-to-noise ratio.

These new software capabilities have been used to gain additional understanding of tunneling spectroscopy of molybdenum disulfide (MoS_2). MoS_2 is a layered semiconducting transition-metal dichalcogenide which has been extensively studied in our group(4). Pixel-correlated current-voltage spectra (i-v's) obtained in a CITS study of its cleavage surface have been used to isolate the source of a feature intermittently present in our tunneling spectra of MoS_2 , negative differential resistance (NDR). NDR is characterized by a decrease in current magnitude which occurs as the tip-sample voltage is increased. It occurs when a peak exists in the electronic density of states of both the tip and the surface within the energy range of the i-v curve(5). The effect has been exploited in a number of electronic devices to make amplifiers, fast switches, and oscillators(6).

f. Brief summary of plans for next years work:

Our results on imaging DNA demonstrate the great potential of STM for the characterization of biomolecular structures and support the possibility of using the technique to sequence DNA. However, we must first develop a technique for DNA sample preparation that is reliable and clean. We propose to use STM to study the structure of interesting or novel nucleic acid-based structures, such as the cruciform observed in DNA recombination, triple-stranded DNA, labeled or "tagged" single-stranded DNA and DNA-protein binding structures.

We have recently designed and constructed a low-cost molecular-beam-epitaxy (MBE) system to be incorporated into our existing UHV-STM system. We propose to use the MBE system to prepare epitaxial films for structural and electronic investigations with STM. Both homoepitaxial and heteroepitaxial films of silicon and gallium arsenide will be studied.

Organic molecules containing either a hydroxy or carboxy group react with the silicon(111) 7x7 surface by reaction with the oxygen atom and subsequent dissociative adsorption at room temperature. Methanol, ethanol, as well as formic acid (HCO_2H), propanoic acid ($\text{CH}_3\text{CH}_2\text{CO}_2\text{H}$), acrylic acid ($\text{CH}_2=\text{CHCO}_2\text{H}$), propiolic acid ($\text{HC}\equiv\text{CCO}_2\text{H}$) and the corresponding alcohols are ideally suited for STM studies as they are covalently bound to the surface, minimizing molecular motion.

We also propose to develop a new spectroscopic technique, Current Imaging Separation Spectroscopy. Images of tunneling current at selected separations between the tip and the sample can then be constructed showing spatial variations in the electronic density of states at a given energy. This technique will be applied to study the site-specific spectroscopy of MoTe_2 , a transition metal dichalcogenide similar to MoS_2 , and a CISS study will test the predictions of theoretical models for these materials by simultaneously acquiring current data at tip-sample separations ranging through the calculated transition region. We are also seeking to put on a firm basis the mechanism for the contrast which we observe in imaging molecular species physisorbed on surfaces. Finally, we propose to complete the construction of an Atomic Force Microscope (AFM) and apply this system to the study of polymers and biological molecules.

References:

1. R. J. Driscoll, M. G. Youngquist, J. D. Baldeschwieler "Atomic-Scale Imaging DNA Using Scanning Tunneling Microscopy," to be published in *Nature* (1990).
2. R. J. Driscoll, M. G. Youngquist, J. D. Baldeschwieler *Bull.Am.Phys.Soc.* 35(3), 649 (1990).
3. R. M. Tromp, R. J. Hamers, J. E. Demuth *Science* 234, 304-309 (1986).
4. M. Weimer, J. Kramar, C. Bai, J. D. Baldeschwieler *Phys.Rev. B* 37, 4292-4295 (1990); J. Kramar S. Baker, R. Driscoll, M. Weimer, J. Baldeschwieler, W. Kaiser, poster presentation, 3rd International Conf. on STM, Oxford, England (1988).
5. I-W Lyo, Ph. Avouris *Science* 245, 1369-1371 (1989).
6. S. M. Sze, *The Physics of Semiconductor Devices*, Wiley-Interscience, New York (1981).

g. List of graduate students currently working on project:

**Shenda Baker
David Baselt
Terry Coley**

**Robert Driscoll
Michael Youngquist**

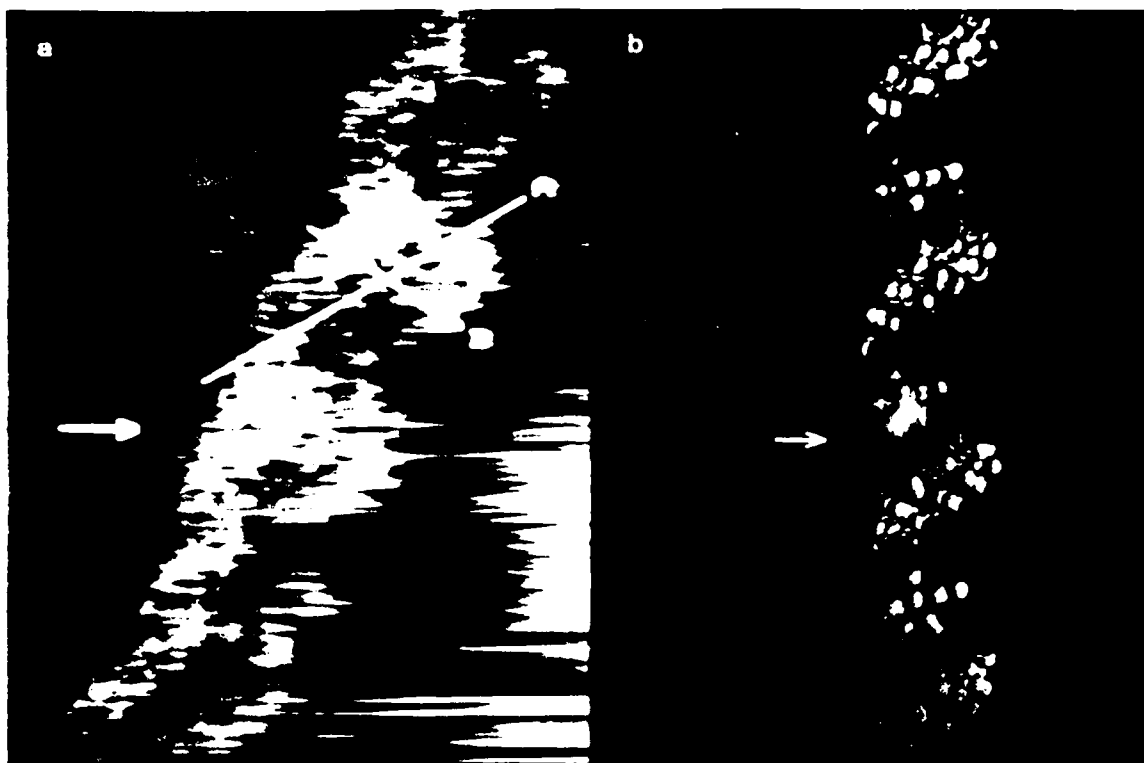


Figure 1. a) Unsmoothed, unfiltered plane-subtracted STM image of DNA $\sim 80 \times 120$ Å. Yellow represents topographic maxima. The parallel bands (several of which are marked with red arrows) at 18° to the helix axis are base pairs in the minor grooves. During a brief tip instability (central arrow), the probe tip may have tilted the DNA molecule. Lines labeled A and B are directions of cross-sections taken through the STM data, shown in Figure 4 of this report. b) A corresponding section of a van der Waals model of A-DNA, in which the phosphate-sugar backbone is red and the base pairs are yellow.

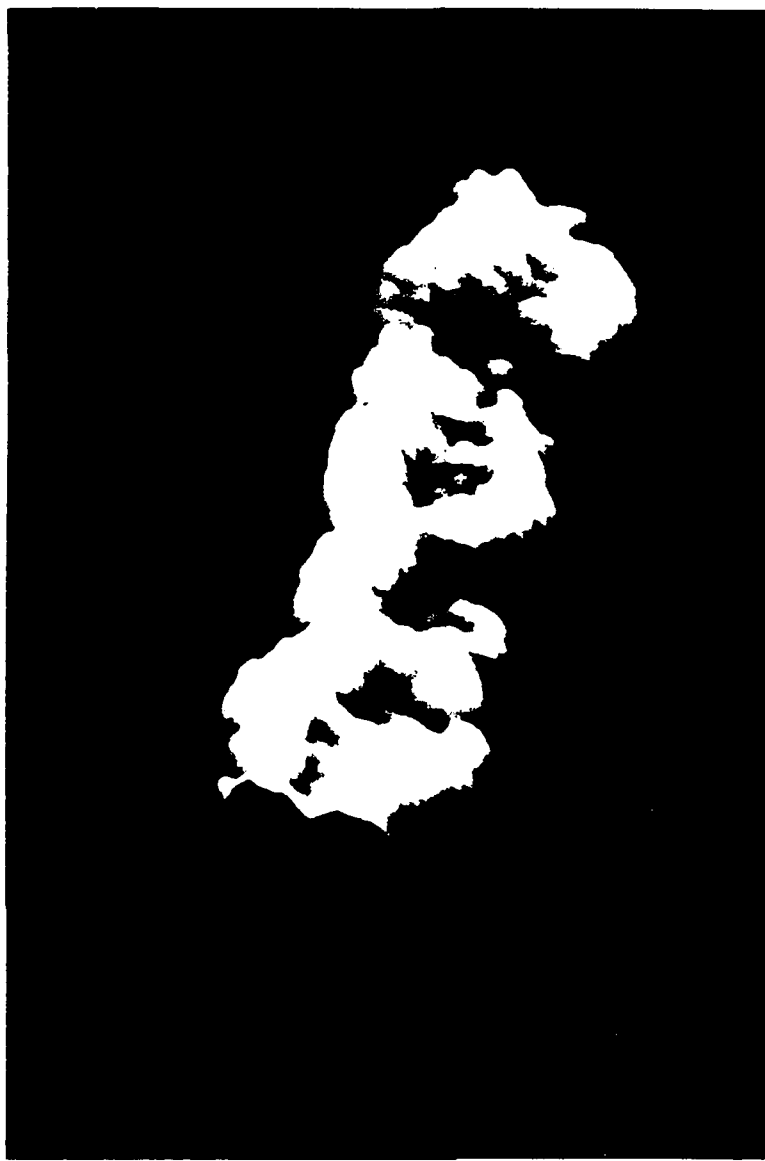


Figure 2. A solid-modeled perspective representation of the data from Figure 1a of this report. The image is $\sim 50 \times 100$ Å in size and has been smoothed over an area ~ 0.6 Å on a side FWHM. This image represents a magnification of $\sim 10,000,000$ times.

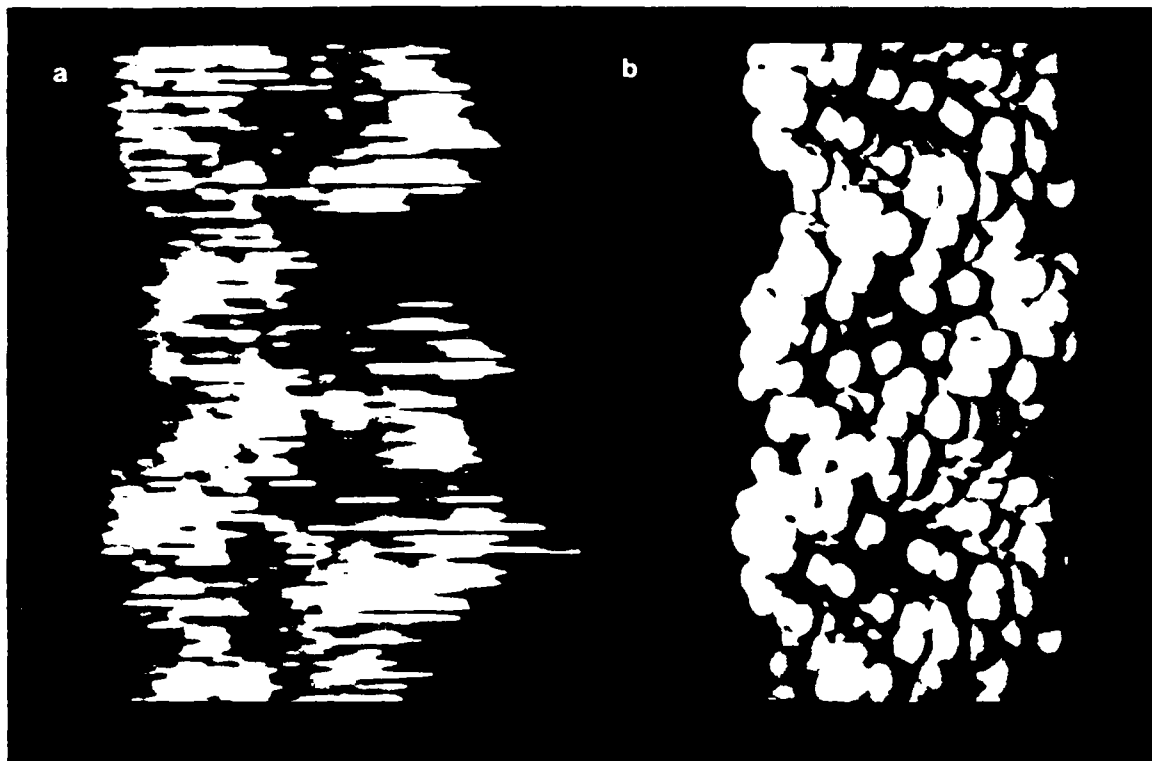


Figure 3. Comparison of the bottom portion of Figure 1a with a corresponding section of a van der Waals model of A-DNA. The STM image is $\sim 35 \times 55 \text{ \AA}$ and shows nearly two helical turns. The y axis is skewed several degrees to facilitate direct comparison. Hydrogen atoms of the model are omitted for clarity.

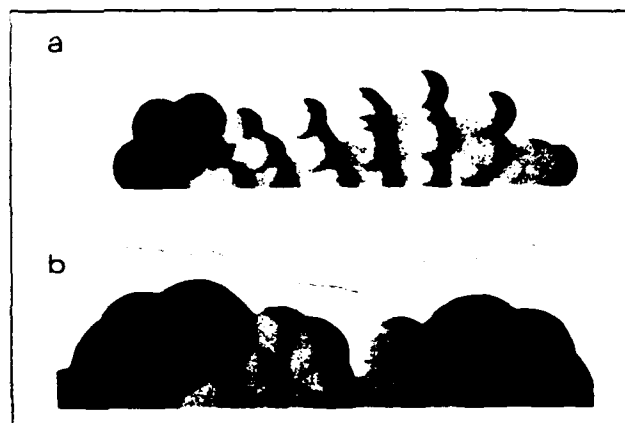


Figure 4. Interpolated experimental STM tip trajectories following lines A and B in Figure 1a of this report compared to the atomic contours of an A-DNA van der Waals surface model. In each case, the experimental cross-section is placed above the corresponding region of the model. In a), representing line A, a cut across the base pair planes approximating the minor groove axis is shown. Starting at the left, the line cuts through the phosphate-sugar backbone (red) on the leading edge and shows the base pair (yellow) periodicity across the groove. In b), line B cuts across the minor groove through the two high backbones and an intermediate base pair. The data were smoothed using a binomially weighted sliding window average, corresponding to a 2-dimensional Gaussian of $\sim 0.60 \text{ \AA}$ FWHM.

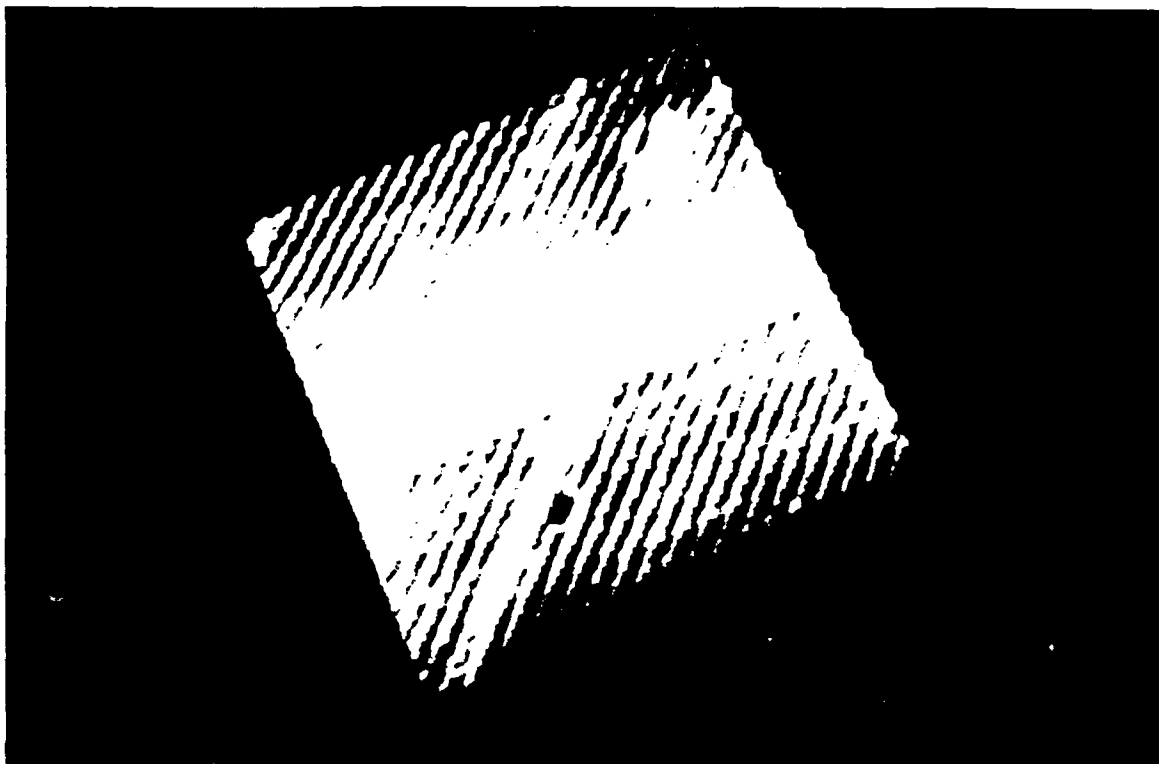


Figure 5. A topographical image of n-type GaAs $\sim 100 \times 100 \text{ \AA}$ showing rows of arsenic atoms running diagonally. The sample bias is negative so that filled surface states of arsenic atoms are accessed. Two point defects, caused by missing arsenic atoms, are clearly seen in the lower left and upper right corners. Note that the spatial extent of point defects is localized to their locations in the surface lattice.

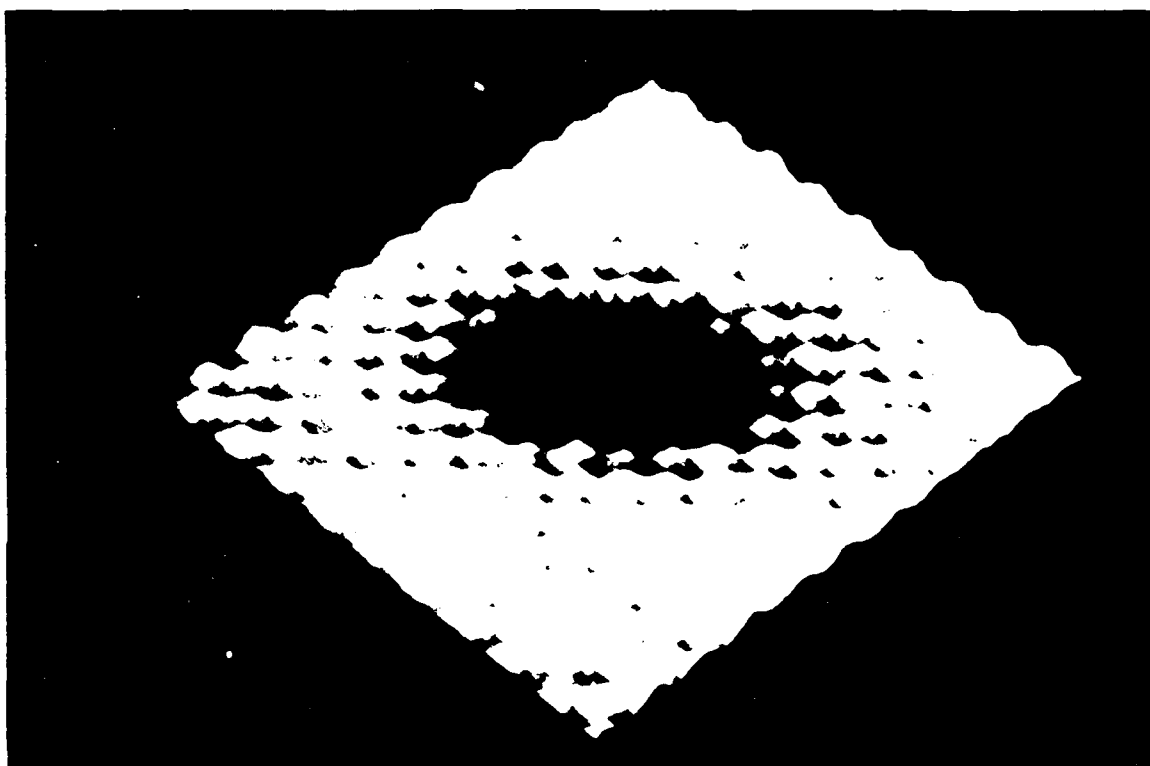


Figure 6. A topographical image of n-GaAs $\sim 50 \times 50 \text{ \AA}$ taken at positive sample bias, showing the empty states of gallium atoms on the surface. The large "hole" in the center of the image is caused by an adsorbed contaminant atom, presumably oxygen, producing a deficiency of electron density in the vicinity of the contaminant. Note that this electronic screening effect, in contrast to point defects, extends spatially a large distance from the adsorption site.

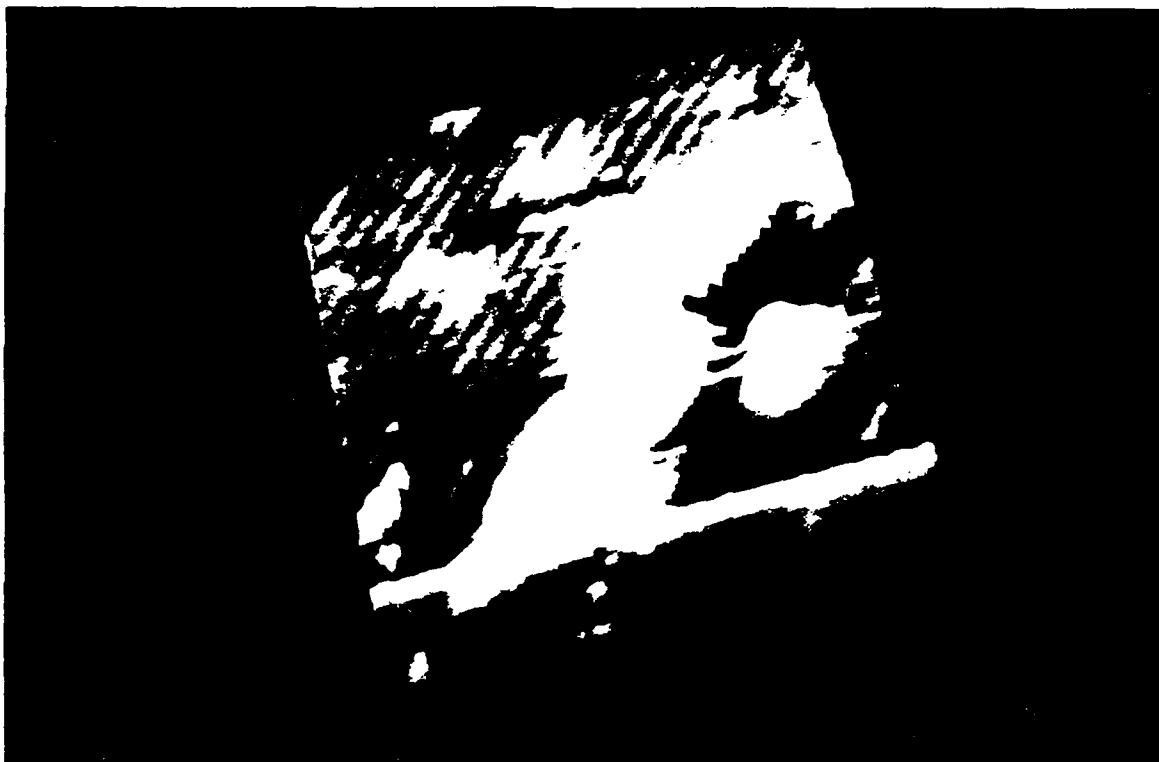


Figure 7. A topographical STM image of arsenic atoms on the surface of n-GaAs. The image is $\sim 100 \times 100 \text{ \AA}$ and shows a tip change about one-fifth from the bottom of the image along with a number of "contaminant" clusters and a large hole approximately 25 \AA in diameter.

PART III

SCANNING TUNNELING MICROSCOPY (STM)

- based on quantum-mechanical phenomenon of tunneling
- **non-destructive *real-space*** topographic and spectroscopic imaging technique
- atomic-scale resolution
 - lateral: 1 - 2 Å
 - vertical: 0.01 - 0.1 Å
- potentially applicable to study of biological adsorbates like DNA

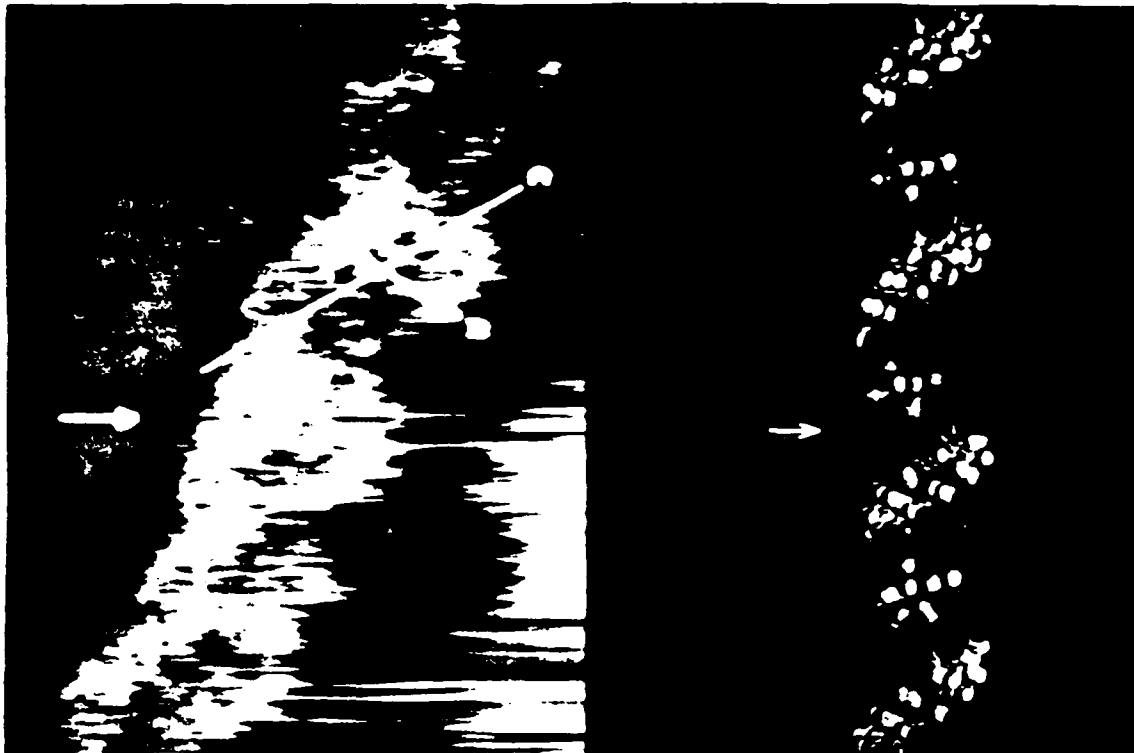


FIGURE 1

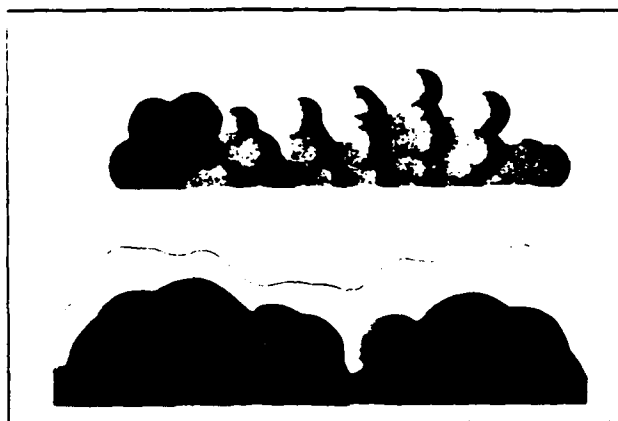


FIGURE 2

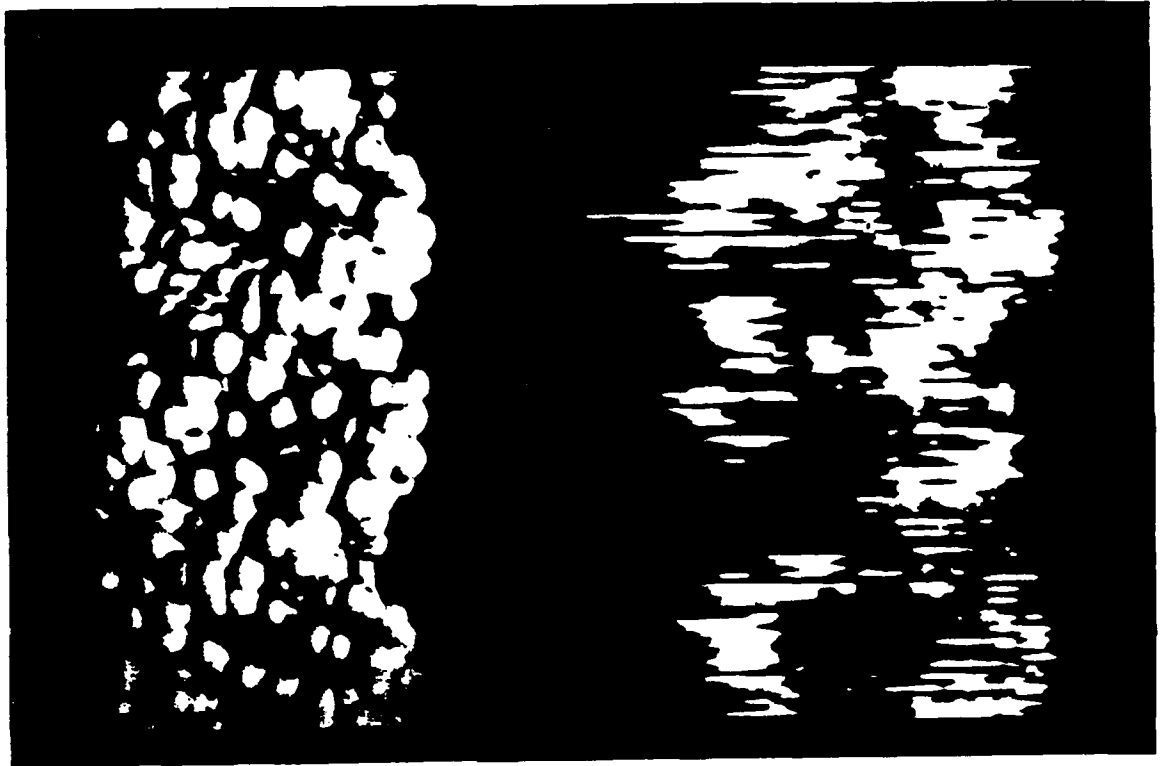


FIGURE 3

STM OF DNA

- DNA double-helix visualized for first time on atomic scale
- highest resolution on single DNA molecule by any technique to date
- STM permits study of *local* structure on *individual* molecules (not possible with X-ray crystallography)
- STM experimental contours agree with model on atomic scale
- STM image dimensions correlate well with X-ray crystallography:

	<u>STM</u>	<u>X-RAY</u>
Helix Pitch	29 Å	28.5 Å
Minor Groove Width	10 Å	11.0 Å
Major Groove Width	3 Å	2.7 Å
Molecular Width	23 Å	23 Å
Phosphate Backbone Width	10 Å	11.6 Å
Axial Nucleotide Rise	2.6 Å	2.59 Å
Base Pair Angle	+ 18°	+ 19°
Helix Symmetry	11	11.0

- FIGURE 1.** Raw data image $80 \times 120 \text{ \AA}$ of individual DNA molecule, where yellow represents topographic maxima. The parallel bands at 18° to the helix axis are base pairs in the minor grooves, several of which are indicated by red arrows. During a brief instability (see central arrow), the probe tip did not retract over the molecule.
- FIGURE 2.** Experimental tip trajectories for cross-sections A and B in Figure 1, compared to A-DNA van der Waals model based on X-ray crystallographic data. The model shows the phosphate-sugar backbone in red; the base pair atoms are yellow. **A:** across the base pair planes approximating the minor groove axis. **B:** across the minor groove and an intermediate base pair. Height and length are on same scale. Hydrogen atoms are omitted for clarity. The comparison shows the remarkable agreement between the STM cross-sections and the model.
- FIGURE 3.** A $35 \times 55 \text{ \AA}$ raw data image of the bottom portion of Figure 1 compared to a van der Waals model. Contrast has been enhanced by histogram equalization. The y axis is skewed by several degrees to facilitate direct comparison. Hydrogens are again omitted.